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(54) Title: CATALYSTS, METHOD OF PREPARING THESE CATALYSTS, AND POLYMERIZATION PROCESSES WHEREIN THESE CATALYSTS ARE USED			
(57) Abstract			
<p>A catalyst is prepared by combining a bis(cyclopentadienyl)zirconium compound with a second compound comprising a cation capable of donating a proton and a bulky, labile anion comprising a plurality of boron atoms capable of stabilizing the zirconium cation formally having a coordination number of 3 and a valence of +4 which is formed as a result of the combination. Many of the catalysts thus formed are stable and isolable and may be recovered and stored. The catalysts may be preformed and then used to polymerize olefins or the catalysts may be formed in situ during polymerization by adding the separate components to the polymerization reaction. The catalyst will be formed when the two components are combined at a temperature within the range from about -100°C to about 300°C. The catalysts thus prepared afford better control of polymer molecular weight and are not subject to equilibrium reversal. The catalysts thus produced are also less pyrophoric than the more conventional Ziegler-Natta olefin polymerization catalysts.</p>			

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CATALYSTS, METHOD OF PREPARING THESE CATALYSTS,  
AND POLYMERIZATION PROCESSES WHEREIN THESE CATALY  
STS ARE USED

1        This is a Continuation-in-Part of U. S. Patent Application  
2        Serial No. 011,471, filed January 30, 1987.

3        BACKGROUND OF THE INVENTION

4        This invention relates to compositions of matter useful as  
5        catalysts, to a method for preparing these catalysts, to a process  
6        wherein these compositions of matter are used as catalysts and to  
7        polymeric products produced with these catalysts. More  
8        particularly, this invention relates to catalyst compositions, to a  
9        method of making said catalyst compositions, to a method for  
10      polymerizing olefins, diolefins and/or acetylenically unsaturated  
11      monomers wherein these catalyst compositions are used, and to  
12      polymeric products produced with these catalyst compositions.

13       The use of soluble Ziegler-Natta type catalysts in the  
14      polymerization of olefins is, of course, well known in the prior  
15      art. In general, these soluble systems comprise a Group IV-B metal  
16      compound and a metal alkyl cocatalyst, particularly an aluminum  
17      alkyl cocatalyst. A subgenus of these catalysts is that subgenus  
18      comprising a bis(cyclopentadienyl) compound of the Group IV-B  
19      metals, particularly titanium, and an aluminum alkyl cocatalyst.  
20       While speculation remains concerning the actual structure of the  
21      active catalyst species in this subgenus of soluble Ziegler-Natta  
22      type olefin polymerization catalysts, it would appear generally  
23      accepted that the active catalyst species is an ion or a  
24      decomposition product thereof which will alkylate an olefin in the  
25      presence of a labile stabilizing anion. This theory may have first  
26      been advocated by Breslow and Newburg, and Long and Breslow, as  
27      indicated in their respective articles appearing in J. Am. Chem.  
28      Soc., 1959, Vol. 81, pp. 81-86, and J. Am. Chem. Soc., 1960, Vol.  
29      82, pp. 1953-1957. As indicated in these articles, various studies  
30      suggested that the active catalyst species is a titanium-alkyl  
31      complex or a species derived therefrom when a titanium compound;  
32      viz., bis(cyclopentadienyl)titanium dihalide, and an aluminum alkyl

1 are used as a catalyst or catalyst precursor. The presence of  
2 ions, all being in equilibrium, when a titanium compound is used  
3 was also suggested by Dyachkovskii, Vysokomol. Soyed., 1965, Vol.  
4 7, pp. 114-115 and by Dyachkovskii, Shilova and Shilov, J. Polym.  
5 Sci., Part C, 1967, pp. 2333-2339. That the active catalyst  
6 species is a cation complex when a titanium compound is used, was  
7 further suggested by Eisch et al., J. Am. Chem. Soc., 1985, Vol.  
8 107, pp. 7219-7221.

9 While the foregoing articles teach or suggest that the  
10 active catalyst species is an ion pair and, particularly an ion  
11 pair wherein the metal component is present as a cation or a  
12 decomposition product thereof, and while these references teach or  
13 suggest coordination chemistry to form such active catalyst  
14 species, all of the articles teach the use of a cocatalyst  
15 comprising a Lewis acid either to form or to stabilize the active  
16 ionic catalyst species. The active catalyst is, apparently, formed  
17 through a Lewis acid-Lewis base reaction of two neutral components  
18 (the metallocene and the aluminum alkyl), leading to an equilibrium  
19 between a neutral, apparently inactive, adduct and an ion pair,  
20 presumably the active catalyst. As a result of this equilibrium,  
21 there is a competition for the anion which must be present to  
22 stabilize the active cation catalyst species. This equilibrium is,  
23 of course, reversible and such reversal will deactivate the  
24 catalyst. Moreover, the catalyst systems heretofore contemplated  
25 are subject to poisoning by the presence of basic impurities in the  
26 system. Further, many, if not all, of the Lewis acids heretofore  
27 contemplated for use in soluble Ziegler-Natta type catalyst systems  
28 are chain transfer agents and, as a result, prevent effective  
29 control of the product polymer molecular weight and product  
30 molecular weight distribution. Still further, most, if not all, of  
31 the cocatalysts heretofore contemplated are highly pyrophoric and,  
32 as a result, somewhat hazardous to use.

33 The aforementioned catalyst systems have not, generally,  
34 been particularly active when zirconium or hafnium is the Group  
35 IV-B metal used. Recently, however, it has been found that active  
36 Ziegler-Natta type catalysts can be formed when bis(cyclo-  
37 pentadienyl)hafnium and bis(cyclopentadienyl)zirconium compounds

1 are used with alumoxanes. As is well known, these systems offer  
2 several distinct advantages, including vastly higher catalytic  
3 activities than the aforementioned bis (cyclopentadienyl)titanium  
4 catalysts and the production of polymers with narrower molecular  
5 weight distributions than those from conventional Ziegler-Natta  
6 catalysts. These systems remain subject to poisoning when basic  
7 impurities are present and do, however, require an undesirable  
8 excess of the alumoxane to function efficiently. Moreover, the  
9 hafnium containing systems are not as active as the zirconium  
10 containing systems, at least when used for homopolymerization.  
11 This has been suggested by Giannetti, Nicoletti, and Mazzocchi, J.  
12 Polym. Sci., Polym. Chem., 1985, Vol. 23, pp. 2117-2133, who  
13 claimed that the ethylene polymerization rates of bis(cyclo-  
14 pentadienyl)hafnium compounds were five to ten times slower than  
15 those of similar bis(cyclopentadienyl)zirconium compounds while  
16 there was little difference between the two catalysts in the  
17 molecular weight of the polyethylene formed from them.

18 In light of the several deficiencies of the coordination  
19 catalyst systems heretofore contemplated, the need for an improved  
20 coordination system which: (1) permits better control of molecular  
21 weight and molecular weight distribution; (2) is not subject to  
22 activation equilibrium; and (3) does not involve the use of an  
23 undesirable cocatalyst is believed readily apparent.

24 SUMMARY OF THE INVENTION

25 It has now been discovered that the foregoing and other  
26 disadvantages of the prior art ionic olefin polymerization  
27 catalysts can be avoided, or at least reduced, with the ionic  
28 catalysts of the present invention and an improved olefin, diolefin  
29 and/or acetylenically unsaturated monomer polymerization process  
30 provided therewith. It is, therefore, an object of this invention  
31 to provide improved ionic catalyst systems useful in the  
32 polymerization of olefins, diolefins and acetylenically unsaturated  
33 monomers. It is another object of this invention to provide a  
34 method for preparing such improved catalysts. It is a further  
35 object of this invention to provide an improved polymerization  
36 process using such improved catalysts. It is still another object  
37 of this invention to provide such an improved catalyst which is not

1 subject to ion equilibrium reversal. It is still a further object  
2 of this invention to provide such an improved catalyst which may  
3 permit better control of the product polymer molecular weight and  
4 molecular weight distribution. It is yet a further object of this  
5 invention to provide such an improved catalyst which may be used  
6 with less risk of fire. It is even another object of this  
7 invention to provide polymeric products produced with these  
8 improved catalysts having relatively narrow molecular weight  
9 distributions and which are free of certain metal impurities. The  
10 foregoing and still other objects and advantages of the present  
11 invention will become apparent from the description set forth  
12 hereinafter and the examples included herein.

13 In accordance with the present invention, the foregoing  
14 and other objects and advantages are accomplished with and by using  
15 a catalyst prepared by combining at least two components, the first  
16 of which is a soluble, bis(cyclopentadienyl)-substituted Group IV-B  
17 metal compound containing at least one ligand which will combine  
18 with a Lewis or Bronsted acid thereby yielding a Group IV-B metal  
19 cation and the second of which compounds comprises a cation capable  
20 of donating a proton and reacting irreversibly with said ligand in  
21 said Group IV-B metal compound to liberate a free, neutral  
22 by-product and a compatible noncoordinating anion comprising a  
23 plurality of boron atoms, which compatible noncoordinating anion is  
24 stable, bulky and labile. The soluble Group IV-B metal compound  
25 must be capable of forming a cation formally having a coordination  
26 number of 3 and a valence of +4 when said ligand is liberated  
27 therefrom. The anion of the second compound must be capable of  
28 stabilizing the Group IV-B metal cation complex without interfering  
29 with the Group IV-B metal cation's or its decomposition product's  
30 ability to function as a catalyst and must be sufficiently labile  
31 to permit displacement by an olefin, a diolefin or an  
32 acetylenically unsaturated monomer during polymerization. For  
33 example, Bochmann and Wilson have reported (J. Chem. Soc., Chem.  
34 Comm., 1986, pp. 1610-1611) that bis(cyclopentadienyl)-titanium  
35 dimethyl reacts with tetrafluoroboric acid to form bis(cyclo-  
36 pentadienyl)titanium methyl tetrafluoroborate. The anion is,  
37 however, insufficiently labile to be displaced by ethylene.

1    DETAILED DESCRIPTION OF THE INVENTION

2       As indicated supra, the present invention relates to  
3       catalysts, to a method for preparing such catalysts, to a method of  
4       using such catalysts and to polymeric products produced with such  
5       catalysts. The catalysts are particularly useful in the  
6       polymerization of  $\alpha$ -olefins, diolefins and acetylenically  
7       unsaturated monomers. The improved catalysts are prepared by  
8       combining at least one first compound which is a bis(cyclo-  
9       pentadienyl) derivative of a metal of Group IV-B of the Periodic  
10      Table of the Elements capable of forming a cation formally having a  
11      coordination number of 3 and a valence of +4 and at least one  
12      second compound comprising a cation capable of donating a proton  
13      and a compatible noncoordinating anion comprising a plurality of  
14      boron atoms, which anion is both bulky and labile, and capable of  
15      stabilizing the Group IV-B metal cation without interfering with  
16      said Group IV-B metal cation's or its decomposition product's  
17      ability to polymerize  $\alpha$ -olefins, diolefins and/or acetylenically  
18      unsaturated monomers.

19      All reference to the Periodic Table of the Elements herein  
20      shall refer to the Periodic Table of the Elements, as published and  
21      copyrighted by CRC Press, Inc., 1984. Also, any reference to a  
22      Group or Groups of such Periodic Table of the Elements shall be to  
23      the Group or Groups as reflected in this Periodic Table of the  
24      Elements.

25      As used herein, the recitation "compatible noncoordinating  
26      anion" means an anion which either does not coordinate to said  
27      cation or which is only weakly coordinated to said cation thereby  
28      remaining sufficiently labile to be displaced by a neutral Lewis  
29      base. The recitation "compatible noncoordinating anion"  
30      specifically refers to an anion which when functioning as a  
31      stabilizing anion in the catalyst system of this invention does not  
32      transfer an anionic substituent or fragment thereof to said cation  
33      thereby forming a neutral four coordinate metallocene and a neutral  
34      boron by-product. Compatible anions are those which are not  
35      degraded to neutrality when the initially formed complex decomposes.

36      The Group IV-B metal compounds, and particularly titanium,  
37      zirconium and hafnium compounds, useful as first compounds in the

1 improved catalyst of this invention are bis(cyclopentadienyl)  
2 derivatives of titanium, zirconium and hafnium. In general, useful  
3 titanium, zirconium and hafnium compounds may be represented by the  
4 following general formulae:

- 5 1.  $(A-Cp)MX_1X_2$
- 6 2.  $(A-Cp)MX'_1X'_2$
- 7 3.  $(A-Cp)ML$
- 8 4.  $(Cp^*)(CpR)MX_1$

9 Wherein:

10 M is a metal selected from the Group consisting of  
11 titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is  
12 either  $(Cp)(Cp^*)$  or  $Cp-A'-Cp^*$  and Cp and Cp<sup>\*</sup> are the  
13 same or different substituted or unsubstituted cyclo-  
14 pentadienyl radicals, wherein A' is a covalent bridging  
15 group containing a Group IV-A element; L is an olefin,  
16 diolefin or aryne ligand; X<sub>1</sub> and X<sub>2</sub> are,  
17 independently, selected from the Group consisting of  
18 hydride radicals, hydrocarbyl radicals having from 1 to  
19 about 20 carbon atoms, substituted-hydrocarbyl radicals,  
20 wherein 1 or more of the hydrogen atoms are replaced with  
21 a halogen atom, having from 1 to about 20 carbon atoms,  
22 organo-metallocid radicals comprising a Group IV-A element  
23 wherein each of the hydrocarbyl substituents contained in  
24 the organo portion of said organo-metallocid,  
25 independently, contain from 1 to about 20 carbon atoms and  
26 the like; X'<sub>1</sub> and X'<sub>2</sub> are joined and bound to the  
27 metal atom to form a metallacycle, in which the metal,  
28 X'<sub>1</sub> and X'<sub>2</sub> form a hydrocarbocyclic ring containing  
29 from about 3 to about 20 carbon atoms; and R is a  
30 substituent, preferably a hydrocarbyl substituent, having  
31 from 1 to about 20 carbon atoms, on one of the  
32 cyclopentadienyl radicals which is also bound to the metal  
33 atom.

34 Each carbon atom in the cyclopentadienyl radical may be,  
35 independently, unsubstituted or substituted with the same or a  
36 different radical selected from the Group consisting of hydrocarbyl  
37 radicals, substituted-hydrocarbyl radicals wherein one or more

1     hydrogen atoms is replaced by a halogen atom, hydrocarbyl-  
2     substituted metalloid radicals wherein the metalloid is selected  
3     from Group IV-A of the Periodic Table of the Elements, halogen  
4     radicals and the like. Suitable hydrocarbyl and substituted-  
5     hydrocarbyl radicals which may be substituted for at least one  
6     hydrogen atom in the cyclopentadienyl radical will contain from 1  
7     to about 20 carbon atoms and include straight and branched alkyl  
8     radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic  
9     hydrocarbon radicals, aromatic radicals and alkyl-substituted  
10    aromatic radicals. Similarly, and when  $X_1$  and/or  $X_2$  is a  
11    hydrocarbyl or substituted-hydrocarbyl radical, each may,  
12    independently, contain from 1 to about 20 carbon atoms and be a  
13    straight or branched alkyl radical, a cyclic hydrocarbyl radical,  
14    an alkyl-substituted cyclic hydrocarbyl radical, an aromatic  
15    radical or an alkyl-substituted aromatic radical. Suitable  
16    organo-metalloid radicals include mono-, di- and trisubstituted  
17    organo-metalloid radicals of Group IV-A elements wherein each of  
18    the hydrocarbyl Groups contains from 1 to about 20 carbon atoms.  
19    Suitable organo-metalloid radicals include trimethylsilyl, tri-  
20    ethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenyl-  
21    germyl, trimethylgermyl and the like.

22    Illustrative, but not limiting examples of bis(cyclo-  
23    pentadienyl)zirconium compounds which may be used in the  
24    preparation of the improved catalyst of this invention are  
25    dihydrocarbyl-substituted bis(cyclopentadienyl)zirconium compounds  
26    such as bis(cyclopentadienyl)zirconium dimethyl,  
27    bis(cyclopentadienyl)zirconium diethyl, bis(cyclopentadienyl)  
28    zirconium dipropyl, bis(cyclopentadienyl)zirconium dibutyl,  
29    bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)  
30    zirconium dineopentyl, bis(cyclopentadienyl)zirconium di(m-tolyl),  
31    bis(cyclopentadienyl)zirconium di(p-tolyl) and the like;  
32    (monohydrocarbyl-substituted cyclopentadienyl)zirconium compounds  
33    such as (methylcyclopentadienyl)(cyclopentadienyl) and  
34    bis(methylcyclopentadienyl)zirconium dimethyl, (ethylcyclo-  
35    pentadienyl)(cyclopentadienyl) and bis(ethylcyclopentadienyl)  
36    zirconium dimethyl, (propylcyclopentadienyl)(cyclopentadienyl) and  
37    bis(propylcyclopentadienyl)zirconium dimethyl, (n-butylcyclo-

1 pentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)  
2 zirconium dimethyl, (t-butylcyclopentadienyl)(cyclopentadienyl) and  
3 bis(t-butylcyclopentadienyl)zirconium dimethyl, (cyclohexylmethyl-  
4 cyclopentadienyl)(cyclopentadienyl) and bis(cyclohexylmethylcyclo-  
5 pentadienyl)zirconium dimethyl, (benzylcyclopentadienyl)  
6 (cyclopentadienyl) and bis(benzylcyclopentadienyl)zirconium  
7 dimethyl, (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and  
8 bis(diphenylmethylcyclopentadienyl)zirconium dimethyl,  
9 (methylcyclopentadienyl)(cyclopentadienyl) and bis(methylcyclo-  
10 pentadienyl)zirconium dihydride, (ethylcyclopenta dienyl)  
11 (cyclopentadienyl) and bis(ethylcyclopentadienyl)zirconium  
12 dihydride, (propylcyclopentadienyl)(cyclopentadienyl) and  
13 bis(propylcyclopentadienyl)zirconium dihydride, (n-butylcyclo-  
14 pentadienyl)(cyclopentadienyl) and bis(n-butylcyclopentadienyl)  
15 zirconium dihydride, (t-butylcyclopentadienyl)(cyclopentadienyl)  
16 and bis(t-butylcyclopentadienyl)zirconium dihydride,  
17 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and  
18 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,  
19 (benzylcyclopentadienyl)(cyclopentadienyl) and bis(benzyl-  
20 cyclopentadienyl)zirconium dihydride, (diphenylmethylcyclo-  
21 pentadienyl)(cyclopentadienyl) and bis(diphenylmethylcyclo-  
22 pentadienyl)zirconium dihydride and the like; (polyhydrocarbyl-  
23 substituted-cyclopentadienyl)zirconium compounds such as  
24 (dimethylcyclopentadienyl)(cyclopentadienyl) and bis(dimethylcyclo-  
25 pentadienyl)zirconium dimethyl, (trimethylcyclopentadienyl)  
26 (cyclopentadienyl) and bis(trimethylcyclopentadienyl)zirconium  
27 dimethyl, (tetramethylcyclopentadienyl)(cyclopentadienyl) and  
28 bis(tetramethylcyclopentadienyl)zirconium dimethyl,  
29 (permethylcyclopentadienyl)(cyclopentadienyl) and bis(permethyl-  
30 cyclopentadienyl)zirconium dimethyl, (ethyltetramethylcyclo-  
31 pentadienyl)(cyclopentadienyl) and bis(ethyltetramethylcyclopentadienyl)  
32 zirconium dimethyl, (indenyl)(cyclopentadienyl) and bis(indenyl)  
33 zirconium dimethyl, (dimethylcyclopentadienyl)(cyclopentadienyl)  
34 and bis(dimethylcyclopentadienyl)zirconium dihydride,  
35 (trimethylcyclopentadienyl)(cyclopentadienyl) and bis(trimethyl-  
36 cyclopentadienyl)zirconium dihydride, (tetramethylcyclo-  
37 pentadienyl)(cyclopentadienyl) and bis(tetramethylcyclo-

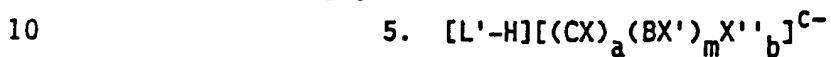
1 pentadienyl)zirconium dihydride, (permethylcyclopentadienyl)  
2 (cyclopentadienyl) and bis(permethylcyclopentadienyl)zirconium  
3 dihydride, (ethyltetramethylcyclopentadienyl)(cyclopentadienyl) and  
4 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,  
5 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride and  
6 the like; (metal hydrocarbyl-substituted cyclopentadienyl)zirconium  
7 compounds such as (trimethylsilylcyclopentadienyl) (cyclopenta-  
8 dienyl) and bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,  
9 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and bis(trimethyl-  
10 germylcyclopentadienyl)zirconium dimethyl, (trimethyl-  
11 stannylcyclopentadienyl)(cyclopentadienyl) and  
12 bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,  
13 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and  
14 bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,  
15 (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and  
16 bis(trimethylsilylcyclopentadienyl)zirconium dihydride,  
17 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and  
18 bis(trimethylgermylcyclopentadienyl)zirconium dihydride,  
19 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and  
20 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,  
21 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and  
22 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the  
23 like; (halogen-substituted-cyclopentadienyl)zirconium compounds  
24 such as (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and  
25 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl,  
26 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and  
27 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the  
28 like; silyl-substituted bis(cyclopentadienyl)zirconium compounds  
29 such as bis(cyclopentadienyl)(trimethylsilyl)(methyl)zirconium,  
30 bis(cyclopentadienyl)(triphenylsilyl)(methyl)zirconium,  
31 bis(cyclopentadienyl)[tris(dimethylsilyl)silyl](methyl)zirconium,  
32 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,  
33 bis(cyclopentadienyl)(trimethylsilyl)(trimethylsilylmethyl)zirconium,  
34 bis(cyclopentadienyl)(trimethylsilyl)(benzyl) and the like;  
35 (bridged-cyclopentadienyl)zirconium compounds such as methylene  
36 bis(cyclopentadienyl)zirconium dimethyl, ethylene  
37 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl

1       bis(cyclopentadienyl)zirconium dimethyl, methylene bis(cyclopentadienyl)zirconium dihydride, ethylene bis(cyclopentadienyl)zirconium dihydride and dimethylsilyl bis(cyclopentadienyl)zirconium dihydride and the like; zirconacycles such as bis(pentamethylcyclopentadienyl) zirconacyclobutane, bis(pentamethylcyclopentadienyl) zirconacyclopentane, bis(cyclopentadienyl)zirconaindane and the like; olefin, diolefin and aryne ligand substituted bis(cyclopentadienyl)zirconium compounds such as bis(cyclopentadienyl) (1,3-butadiene)zirconium, bis(cyclopentadienyl) (2,3-dimethyl-1,3-butadiene)zirconium, bis(pentamethylcyclopentadienyl)(benzyne) zirconium and the like; (hydrocarbyl)(hydride) bis(cyclopentadienyl)zirconium compounds such as bis(pentamethylcyclopentadienyl)zirconium (phenyl)(hydride), bis(pentamethylcyclopentadienyl)zirconium (methyl)(hydride) and the like; and bis(cyclopentadienyl)zirconium compounds in which a substituent on the cyclopentadienyl radical is bound to the metal such as (pentamethylcyclopentadienyl)(tetramethylcyclopentadienylmethylen) zirconium hydride, (pentamethylcyclopentadienyl)(tetramethylcyclopentadienylmethylen) zirconium phenyl and the like.

20       A similar list of illustrative bis(cyclopentadienyl) hafnium and bis(cyclopentadienyl)titanium compounds could be made, 21 but since the lists would be nearly identical to that already 22 presented with respect to bis(cyclopentadienyl)zirconium compounds, 23 such lists are not deemed essential to a complete disclosure. 24 Those skilled in the art, however, are aware that bis(cyclopentadienyl)hafnium compounds and bis(cyclopentadienyl) titanium 25 compounds corresponding to certain of the bis(cyclopentadienyl) 26 zirconium compounds listed supra are not known. The lists would, 27 therefore, be reduced by these compounds. Other bis(cyclopentadienyl)hafnium compounds and other bis(cyclopentadienyl)titanium 28 compounds as well as other bis(cyclopentadienyl)zirconium compounds 29 which are useful in the catalyst compositions of this invention 30 will, of course, be apparent to those skilled in the art.

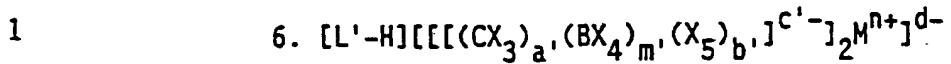
34       Compounds useful as a second component in the preparation 35 of the catalyst of this invention will comprise a cation, which is 36 a Bronsted acid capable of donating a proton, and a compatible

1 anion containing a plurality of boron atoms, which anion is  
2 relatively large, capable of stabilizing the active catalyst  
3 species which is formed when the two compounds are combined and  
4 said anion will be sufficiently labile to be displaced by olefinic,  
5 diolefinic and acetylenically unsaturated substrates or other  
6 neutral Lewis bases such as ethers, nitriles and the like. In  
7 general, a second compound useful in the preparation of the  
8 catalysts of this invention may be any compound represented by one  
9 of the following general formulae:



11 Wherein:

12  $L'-H$  is either  $H^+$ , ammonium or a substituted ammonium  
13 cation having up to 3 hydrogen atoms replaced with a  
14 hydrocarbyl radical containing from 1 to about 20 carbon  
15 atoms or a substituted-hydrocarbyl radical, wherein one or  
16 more of the hydrogen atoms is replaced by a halogen atom,  
17 containing from 1 to about 20 carbon atoms, phosphonium  
18 radicals, substituted-phosphonium radicals having up to 3  
19 hydrogen atoms replaced with a hydrocarbyl radical  
20 containing from 1 to about 20 carbon atoms or a  
21 substituted-hydrocarbyl radical, wherein 1 or more of the  
22 hydrogen atoms is replaced by a halogen atom, containing  
23 from 1 to about 20 carbon atoms and the like; B and C are,  
24 respectively, boron and carbon; X,  $X'$  and  $X''$  are radicals  
25 selected, independently, from the Group consisting of  
26 hydride radicals, halide radicals, hydrocarbyl radicals  
27 containing from 1 to about 20 carbon atoms,  
28 substituted-hydrocarbyl radicals, wherein one or more of  
29 the hydrogen atoms is replaced by a halogen atom,  
30 containing from 1 to about 20 carbon atoms, organo-  
31 metalloid radicals wherein each hydrocarbyl substitution  
32 in the organo portion contains from 1 to about 20 carbon  
33 atoms and said metal is selected from Group IV-A of the  
34 Periodic Table of the Elements and the like; a and b are  
35 integers  $\geq 0$ ; c is an integer  $\geq 1$ ;  $a + b + c =$  an  
36 even-numbered integer from 2 to about 8; and m is an  
37 integer ranging from 5 to about 22.



2                   Wherein:

3                   L'-H is either  $H^+$ , ammonium or a substituted ammonium  
4                   radical having up to 3 hydrogen atoms replaced with a  
5                   hydrocarbyl radical containing from 1 to about 20 carbon  
6                   atoms or a substituted-hydrocarbyl radical, wherein 1 or  
7                   more of the hydrogen atoms is replaced by a halogen atom,  
8                   containing from 1 to about 20 carbon atoms, a phosphonium  
9                   radical, a substituted-phosphonium radical having up to 3  
10                  hydrogen atoms replaced with a hydrocarbyl radical  
11                  containing from 1 to about 20 carbon atoms or a  
12                  substituted-hydrocarbyl radical, wherein 1 or more of the  
13                  hydrogen atoms is replaced by a halogen atom, containing  
14                  from 1 to about 20 carbon atoms and the like; B, C, M and  
15                  H are, respectively, boron; carbon, a transition metal and  
16                  hydrogen;  $X_3$ ,  $X_4$ , and  $X_5$  are radicals selected,  
17                  independently, from the Group consisting of hydride  
18                  radicals, halide radicals, hydrocarbyl radicals containing  
19                  from 1 to about 20 carbon atoms, substituted-hydrocarbyl  
20                  radicals, wherein one or more of the hydrogen atoms is  
21                  replaced by a halogen atom, containing from 1 to about 20  
22                  carbon atoms, organo-metallloid radicals wherein each  
23                  hydrocarbyl substitution in the organo portion or said  
24                  organo-metallloid contains from 1 to about 20 carbon atoms  
25                  and said metal is selected from Group IV-A of the Periodic  
26                  Table of the Elements and the like;  $a'$  and  $b'$  are the same  
27                  or a different integer  $\geq 0$ ;  $c'$  is an integer  $\geq 2$ ;  
28                   $a' + b' + c' =$  an even-numbered integer from 4 to about 8;  
29                   $m'$  is an integer from 6 to about 12;  $n$  is an integer such  
                        that  $2c' - n = d$ ; and  $d$  is an integer  $\geq 1$ .

30                  Illustrative, but not limiting, examples of the second  
31                  compounds which can be used as a second component in the catalyst  
32                  compositions of this invention are ammonium salts such as ammonium  
33                  1-carbadodecaborate (using 1-carbadodecaborate as an illustrative,  
34                  but not limiting, counterion for the ammonium cations listed  
35                  below): monohydrocarbyl-substituted ammonium salts such as  
36                  methylammonium 1-carbadodecaborate, ethylammonium 1-carbadode-

1 caborate, propylammonium 1-carbadodecaborate, isopropylammonium  
2 1-carbadodecaborate, (n-butyl)ammonium 1-carbadodecaborate,  
3 anilinium 1-carbadodecaborate, and (p-tolyl)ammonium  
4 1-carbadodecaborate and the like; dihydrocarbyl-substituted  
5 ammonium salts such as dimethylammonium 1-carbadodecaborate,  
6 diethylammonium 1-carbadodecaborate, dipropylammonium  
7 1-carbadodecaborate, diisopropylammonium 1-carbadodecaborate,  
8 di(n-butyl)ammonium 1-carbadodecaborate, diphenylammonium  
9 1-carbadodecaborate, di(p-tolyl)ammonium 1-carbadodecaborate and  
10 the like; trihydrocarbyl-substituted ammonium salts such as  
11 trimethylammonium 1-carbadodecaborate, triethylammonium  
12 1-carbadodecaborate, tripropylammonium 1-carbadodecaborate,  
13 tri(n-butyl) ammonium 1-carbadodecaborate, triphenylammonium  
14 1-carbadodecaborate, tri(p-tolyl)ammonium 1-carbadodecaborate,  
15 N,N-dimethylanilinium 1-carbadodecaborate, N,N-diethylanilinium  
16 1-carbadodecaborate and the like.

17 Illustrative, but not limiting examples of second  
18 compounds corresponding to Formula 5 [using tri(n-butyl)ammonium as  
19 an illustrative, but not limiting, counterion for the anions listed  
20 below] are salts of anions such as bis[tri(n-butyl)ammonium]  
21 nonaborate, bis[tri(n-butyl)ammonium]decaborate,  
22 bis[tri(n-butyl)ammonium]undecaborate, bis[tri(n-butyl)ammonium]  
23 dodecaborate, bis[tri(n-butyl)ammonium]decachlorodecaborate,  
24 bis[tri(n-butyl)ammonium]dodecachlorododecaborate,  
25 tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium  
26 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate,  
27 tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate,  
28 tri(n-butyl)ammonium dibromo-1-carbadodecaborate and the like;  
29 borane and carborane complexes and salts of borane and carborane  
30 anions such as decaborane(14), 7,8-dicarbaundecaborane(13),  
31 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-  
32 dicarbaundecaborane, dodecahydrido-11-methyl-2,7-di-  
33 carbaundecaborane, tri(n-butyl)ammonium undecaborate(14),  
34 tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium  
35 7-carbaundecaborate(13), tri(n-butyl)ammonium 7,8-dicarbaunde-  
36 caborate(12), tri(n-butyl)ammonium 2,9-dicarbaundecaborate(12),  
37 tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaunde-

1 caborate, tri(n-butyl)ammonium undecahydrido-8-ethyl-  
2 7,9-dicarbaundecaborate, tri(n-butyl)ammonium undecahydrido-  
3 8-butyl-7,9-dicarbaundecaborate, tri(n-butyl)ammonium  
4 undecahydrido-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl)ammonium  
5 undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate,  
6 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate  
7 and the like; boranes and carboranes and salts of boranes and  
8 carboranes such as 4-carbanonaborane(14), 1,3-dicarbanona-  
9 borane(13), 6,9-dicarbadecaborane(14), dodecahydrido-1-  
10 phenyl-1,3-dicarbanonaborane, dodecahydrido-1-methyl-1,3-  
11 dicarbanonaborane, undecahydrido-1,3-dimethyl-1,3-dicarbanona-  
12 borane and the like.

13 Illustrative, but not limiting, examples of second  
14 compounds corresponding to Formula 6 [using tri(n-butyl)ammonium as  
15 an illustrative, but not limiting, counterion for the anions listed  
16 below] are salts of metallacarborane and metallaborane anions such  
17 as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborato)  
18 cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-  
19 dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(undeca-  
20 hydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)  
21 ammonium bis(undecahydrido-7,8-dicarbaundecaborato) nickelate(III),  
22 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)  
23 cuprate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicar-  
24 baundecaborato)aurate(III), tri(n-butyl)ammonium bis(nonahydrido-  
25 7,8-dimethyl-7,8-dicarbaundecaborato)-ferrate(III), tri(n-butyl)  
26 ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)  
27 chromate(III), tri(n-butyl)ammonium bis(tribromo-octahydrido-  
28 7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium  
29 bis(dodecahydridodicarbadecaborato)cobaltate(III),  
30 bis[tri(n-butyl)ammonium] bis(dodecahydridodecaborato)  
31 nickelate(II), tris[tri(n-butyl)ammonium] bis(undecahydrido-7-  
32 carbaundecaborato)chromate(III), bis[tri(n-butyl) ammonium]  
33 bis(undecahydrido-7-carbaundecaborato)manganate(IV),  
34 bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)  
35 cobaltate(III), bis[tri(n-butyl)ammonium] bis(undecahydrido-7-  
36 carbaundecaborato)nickelate(IV) and the like. A similar list of  
37 representative phosphonium compounds could be recited as

1       illustrative second compounds, but for the sake of brevity, it is  
2       simply noted that the phosphonium and substituted-phosphonium salts  
3       corresponding to the listed ammonium and substituted-ammonium salts  
4       could be used as second compounds in the present invention.

5       In general, and while most first components identified  
6       above may be combined with most second components identified above  
7       to produce an active olefin polymerization catalyst, it is  
8       important to continued polymerization operations that either the  
9       initially formed metal cation or a decomposition product thereof be  
10      a relatively stable olefin polymerization catalyst. It is also  
11      important that the anion of the second compound be stable to  
12      hydrolysis when an ammonium salt is used. Further, it is important  
13      that the acidity of the second component be sufficient, relative to  
14      the first, to facilitate the needed proton transfer. Conversely,  
15      the basicity of the metal complex must also be sufficient to  
16      facilitate the needed proton transfer. Certain metallocene  
17      compounds--using bis(pentamethylcyclopentadienyl)hafnium dimethyl  
18      as an illustrative, but not limiting example--are resistant to  
19      reaction with all but the strongest Bronsted acids and thus are not  
20      suitable as first components to form the catalysts described  
21      herein. In general, bis(cyclopentadienyl)metal compounds which can  
22      be hydrolyzed by aqueous solutions can be considered suitable as  
23      first components to form the catalysts described herein.

24      With respect to the combination of the desired cation and  
25      the stabilizing anion to form an active catalyst of the present  
26      invention, it should be noted that the two compounds combined for  
27      preparation of the active catalyst must be selected so as to ensure  
28      displacement of the anion by monomer or another neutral Lewis  
29      base. This could be done by steric hindrance, resulting from  
30      substitutions on the cyclopentadienyl carbon atoms as well as from  
31      substitutions on the anion itself. The use of perhydrocarbyl-  
32      substituted cyclopentadienyl metal compounds and/or bulky second  
33      components does not generally prevent the desired combination and,  
34      in fact, generally yields more labile anions. It follows, then,  
35      that metal compounds (first components) comprising perhydrocarbyl-  
36      substituted cyclopentadienyl radicals could be effectively used  
37      with a wider range of second compounds than could metal compounds

1 (first components) comprising unsubstituted cyclopentadienyl  
2 radicals. In fact, first compounds comprising perhydrocarbyl-  
3 substituted cyclopentadienyl radicals would, generally, be  
4 effective when used in combination with second components having  
5 both larger and smaller anions. As the amount and size of the  
6 substitutions on the cyclopentadienyl radicals are reduced,  
7 however, more effective catalysts are obtained with second  
8 compounds containing larger anions, such as those encompassed by  
9 Equation 6 above and those having larger  $m$  values in Equation 5.  
10 In these cases, it is further preferable that in using second  
11 compounds which are encompassed by Equation 5,  $a + b + c = 2$ .  
12 Second compounds in which  $a + b + c =$  even-numbered integers of 4  
13 or more have acidic B-H-B moieties which can react further with the  
14 metal cation formed, leading to catalytically inactive compounds.

15 In general, the catalyst can be prepared by combining the  
16 two components in a suitable solvent at a temperature within the  
17 range from about -100°C to about 300°C. The catalyst may be used  
18 to polymerize  $\alpha$ -olefins and acetylenically unsaturated monomers  
19 having from two to about eighteen carbon atoms and diolefins having  
20 from four to about eighteen carbon atoms either alone or in  
21 combination. The catalyst may also be used to polymerize  
22  $\alpha$ -olefins, diolefins and/or acetylenically unsaturated monomers  
23 in combination with other unsaturated monomers. In general, the  
24 polymerization will be accomplished at conditions well known in the  
25 prior art for the polymerization of monomers of this type. It  
26 will, of course, be appreciated that the catalyst system will form  
27 in situ if the components thereof are added directly to the  
28 polymerization process and a suitable solvent or diluent is used in  
29 said polymerization process. It is, however, preferred, to form  
30 the catalyst in a separate step prior to adding the same to the  
31 polymerization step. While the catalysts do not contain pyrophoric  
32 species, the catalyst components are sensitive to both moisture and  
33 oxygen and should be handled and transferred in an inert atmosphere  
34 such as nitrogen, argon or helium.

35 As indicated supra, the improved catalyst of the present  
36 invention will, generally, be prepared in a suitable solvent or  
37 diluent. Suitable solvents or diluents include any of the solvents

1 known in the prior art to be useful as solvents in the  
2 polymerization of olefins. Suitable solvents, then, include, but  
3 are not necessarily limited to, straight and branched-chain  
4 hydrocarbons such as isobutane, butane, pentane, hexane, heptane,  
5 octane and the like, cyclic and alicyclic hydrocarbons such as  
6 cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane  
7 and the like and aromatic and alkyl substituted aromatic compounds  
8 such as benzene, toluene, xylene and the like. Suitable solvents  
9 also include basic solvents not heretofore useful as polymerization  
10 solvents when conventional Ziegler-Natta type polymerization  
11 catalysts are used such as chlorobenzene, dichloromethane and  
12 propyl chloride.

13 While the inventors do not wish to be bound by any  
14 particular theory, it is believed that when the two compounds used  
15 to prepare the improved catalysts of the present invention are  
16 combined in a suitable solvent or diluent, all or a part of the  
17 cation of the second compound (the proton) combines with one of the  
18 substituents on the metal-containing (first) component. In the  
19 case where the first component has a formula corresponding to that  
20 of general formula 1 supra, a neutral compound is liberated which  
21 either remains in solution or is liberated as a gas. In this  
22 regard, it should be noted that if the cation of the second  
23 compound is a proton and either  $X_1$  or  $X_2$  in the metal  
24 containing (first) compound is a hydride, hydrogen gas may be  
25 liberated. Similarly, if the cation of the second compound is a  
26 proton and either  $X_1$  or  $X_2$  is a methyl radical, methane may be  
27 liberated as a gas. In the cases where the first component has a  
28 formula corresponding to those of general formulae 2, 3 or 4, one  
29 of the substituents on the metal-containing (first) component is  
30 protonated but, in general, no substituent is liberated from the  
31 metal. It is preferred that the ratio of metal containing (first)  
32 component to second component cations be about 1:1 or greater. The  
33 conjugate base of the cation of the second compound, if such a  
34 portion does remain, will be a neutral compound which will remain  
35 in solution or complex with the metal cation formed, though, in  
36 general, a cation is chosen such that any binding of the neutral  
37 conjugate base to the metal cation will be weak or nonexistent.

1 Thus, as the steric bulk of this conjugated base increases, it  
2 will, simply, remain in solution without interfering with the  
3 active catalyst. For example, if the cation of the second compound  
4 is an ammonium ion, this ion will liberate a hydrogen atom which  
5 may then react as in the case when the hydrogen atom was the cation  
6 to form gaseous hydrogen, methane or the like and the conjugate  
7 base of the cation will be ammonia. In like fashion, if the cation  
8 of the second compound were a hydrocarbyl-substituted ammonium ion  
9 containing at least one hydrogen atom, as is essential to the  
10 present invention, the hydrogen atom would be given up to react in  
11 the same fashion as when hydrogen were the cation and the conjugate  
12 base of the cation would be an amine. Further, if the cation of  
13 the second compound were a hydrocarbyl-substituted phosphonium ion  
14 containing at least one proton, as is essential to the present  
15 invention, the conjugate base of the cation would be phosphine.

16 While still not wishing to be bound by any particular  
17 theory, it is also believed that when the metal containing (first)  
18 component has reacted with the second component, the non-  
19 coordinating anion originally contained in the second compound used  
20 in the catalyst preparation combines with and stabilizes either the  
21 metal cation, formally having a coordination number of 3 and a +4  
22 valence, or a decomposition product thereof. The cation and anion  
23 will remain so combined until the catalyst is contacted with one or  
24 more olefins, diolefins and/or acetylenically unsaturated monomers  
25 either alone or in combination with one or more other monomers. As  
26 indicated supra, the anion contained in the second compound must be  
27 sufficiently labile to permit rapid displacement by an olefin, a  
28 diolefin or an acetylenically unsaturated monomer to facilitate  
29 polymerization.

30 As indicated supra, most first compounds identified above  
31 will combine with most second compounds identified above to produce  
32 an active catalyst, particularly an active polymerization  
33 catalyst. The actual active catalyst species is not, however,  
34 always sufficiently stable as to permit its separation and  
35 subsequent identification. Moreover, and while many of the  
36 initial metal cations are relatively stable, it has become apparent  
37 that the initially formed metal cation may decompose yielding

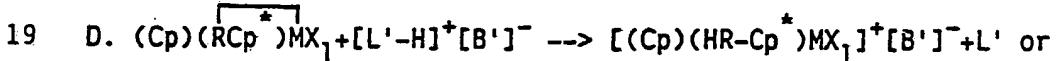
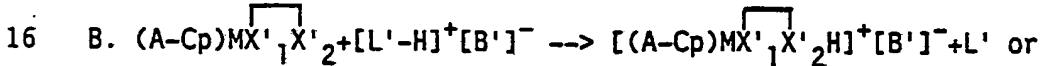
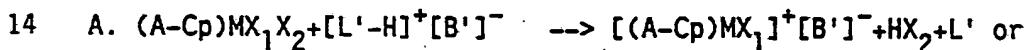
1 either an active polymerization catalyst species or a catalytically  
2 inactive species. Most decomposition products are, however,  
3 catalytically active. While the inventors still do not wish to be  
4 bound by any particular theory, it is believed that the active  
5 catalyst species which have not been isolated, including active  
6 decomposition products, are of the same type as those which have  
7 been isolated and fully characterized or at least retain the  
8 essential structure required for functioning as a catalyst such as  
9 a reactive metal-carbon bond.

10 While still not wishing to be bound by any particular  
11 theory and as indicated supra, it is also believed that the extent  
12 and nature of the substitution on the cyclopentadienyl ring  
13 dictates the size of the stabilizing anion needed to generate a  
14 particularly active olefin polymerization catalyst. In this  
15 regard, it is believed that as the number of substituents on the  
16 cyclopentadienyl radical in the metallocene cation are decreased  
17 from 5 to 0, a given anion will become increasingly less labile.  
18 Thus, it is suggested that as the number of substituents on the  
19 cyclopentadienyl radical in the metallocene cation are reduced from  
20 5 to 0, larger or less reactive anions should be used to ensure  
21 lability and allow for the generation of a particularly active  
22 catalyst species.

23 Consistent with the foregoing, stable, isolable,  
24 characterizable olefin polymerization catalysts have been prepared  
25 when bis(permethylcyclopentadienyl)zirconium dimethyl has been  
26 combined with and reacted with tri(n-butyl)ammonium  
27 7,8-dicarbaundecaborate(12) or 7,8-dicarbaundecaborane(13). A  
28 stable, isolable, olefin polymerization catalyst has also been  
29 prepared when bis(ethyltetramethylcyclopentadienyl)zirconium  
30 dimethyl has been combined with 7,8-dicarbaundecaborane(13). In  
31 each of these cases, the stable polymerization catalyst was  
32 prepared by adding the reactants into a suitable solvent or diluent  
33 at a temperature within the range from about -100°C to about  
34 300°C. Based on this and other information available to the  
35 inventors, it appears clear that isolable and characterizable  
36 polymerization catalysts can also be prepared when a  
37 bis(perhydrocarbyl-substituted cyclopentadienyl)metal compound is

1 combined with any one or more of the second compounds identified  
 2 above. Also, active, but unisolated polymerization catalysts are  
 3 prepared when bis(cyclopentadienyl)zirconium compounds containing  
 4 less than five hydrocarbyl-substitutions on each cyclopentadienyl  
 5 radical are reacted with a suitable second compound, within the  
 6 scope of the present invention, containing a cation capable of  
 7 donating a proton and an anion capable of stabilizing the  
 8 metallocene cation and sufficiently labile to be displaced by an  
 9 olefin, a diolefin or an acetylenically unsaturated monomer during  
 10 polymerization, particularly those second compounds having the  
 11 larger anions.

12 The chemical reactions which occur may be represented by  
 13 reference to the general formulae set forth herein as follows:



21 In the foregoing reaction equations, the letters A-D  
 22 correspond to the numbers 1-4, respectively, set forth in  
 23 combination with the general equations for useful metallocene  
 24 compounds. B' represents a compatible ion corresponding to the  
 25 general formulae outlined in formulae 5 and 6 above. The reaction

1 of each of the four classes of metallocenes with N,N-dimethyl-  
2 anilinium bis(7,8-dicarbaundecaborato)cobaltate(III) has been  
3 examined by solution  $^1\text{H}$  NMR or  $^{13}\text{C}$  NMR spectroscopy. In each  
4 case, products conforming to those outlined above were observed.

5 In general, the stable, isolable catalysts formed by the  
6 method of this invention may be separated from the solvent and  
7 stored for subsequent use. The unisolated catalysts, however,  
8 will, generally, be retained in solution until ultimately used in  
9 the polymerization of olefins. Alternatively, any of the catalysts  
10 prepared by the method of this invention may be retained in  
11 solution for subsequent use or used directly after preparation as a  
12 polymerization catalyst. Moreover, and as indicated supra, the  
13 catalysts may be prepared in situ by passing the separate  
14 components into the polymerization vessel where the components will  
15 be contacted and react to produce the improved catalyst of this  
16 invention.

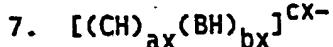
17 In general, and as indicated supra, the improved catalyst  
18 of this invention will polymerize olefins, diolefins and/or  
19 acetylenically unsaturated monomers either alone or in combination  
20 with other olefins and/or other unsaturated monomers at conditions  
21 well known in the prior art for conventional Ziegler-Natta  
22 catalysis. In the polymerization process of this invention, the  
23 molecular weight appears to be a function of both catalyst  
24 concentration, polymerization temperature and polymerization  
25 pressure. In general, the polymers produced with the catalyst of  
26 this invention, when produced in an atmosphere free of hydrogen or  
27 other chain terminating agents, will contain terminal unsaturation.

28 The polymer products produced with the catalyst of this  
29 invention will, of course, be free of certain trace metals  
30 generally found in polymers produced with Ziegler-Natta type  
31 catalysts such as aluminum, magnesium, chloride and the like. The  
32 polymer products produced with the catalysts of this invention  
33 should then have a broader range of applications than polymers  
34 produced with more conventional Ziegler-Natta type catalysts  
35 comprising a metal alkyl, such as an aluminum alkyl.

1      PREFERRED EMBODIMENT OF THE INVENTION

2      In a preferred embodiment of the present invention, a  
 3      polymerization catalyst will be prepared by combining a  
 4      bis(cyclopentadienyl) compound of one of the Group IV-B metals,  
 5      most preferably a bis(cyclopentadienyl)zirconium or  
 6      bis(cyclopentadienyl)hafnium compound, containing two independently  
 7      substituted or unsubstituted cyclopentadienyl radicals and two  
 8      lower alkyl substituents or two hydrides with one of the following:

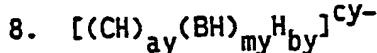
9                (1). A trisubstituted ammonium salt of a borane or  
 10     carborane anion satisfying the general formula:



12     Wherein:

13     B, C, and H are, respectively, boron, carbon and hydrogen;  
 14     ax is either 0 or 1; cx is either 1 or 2; ax + cx = 2; and  
 15     bx is an integer ranging from 10 to 12.

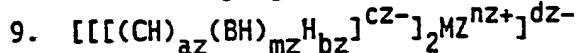
16                (2). A trisubstituted ammonium salt of a borane or  
 17     carborane anion or a neutral borane or carborane compound  
 18     satisfying the general formula:



20     Wherein:

21     B, C and H are, respectively, boron, carbon and hydrogen;  
 22     ay is an integer from 0 to 2; by is an integer from 0 to 3;  
 23     cy is an integer from 0 to 3; ay + by + cy = 4; and my is  
 24     an integer from 9 to 18.

25                (3). A trisubstituted ammonium salt of a metallaborane or  
 26     metallacarborane anion satisfying the general formula:



28     Wherein:

29     B, C, H and MZ are, respectively, boron, carbon, hydrogen  
 30     and a transition metal; az is an integer from 0 to 2; bz  
 31     is an integer from 0 to 2; cz is either 2 or 3;  
 32     mz is an integer from 9 to 11; az + bz + cz = 4; and nz  
 33     and dz are, respectively, 2 & 2 or 3 & 1.

34     Each of the trisubstitutions in the ammonium cation will  
 35     be the same or a different lower alkyl or aryl radical. By lower  
 36     alkyl is meant an alkyl radical containing from one to four carbon

1       atoms. In a most preferred embodiment of the present invention  
2       wherein an anion represented by Formula 7 is used,  
3       bis(pentamethylcyclopentadienyl)zirconium dimethyl will be combined  
4       with tri(n-butyl)ammonium 1-carbaundecaborate to produce a most  
5       preferred catalyst. In a most preferred embodiment of the present  
6       invention wherein an anion represented by Formula 8 is used,  
7       bis(pentamethylcyclopentadienyl)zirconium dimethyl will be combined  
8       with 7,8-dicarbaundecaborane(13) to produce a most preferred  
9       catalyst. In a most preferred embodiment of the present invention  
10      wherein an anion represented by Formula 9 is used,  
11      bis(cyclopentadienyl)zirconium or -hafnium dimethyl will be  
12      combined with N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
13      cobaltate(III) to produce a most preferred catalyst. In a  
14      preferred embodiment of this invention, the two components used to  
15      prepare the catalyst will be combined at a temperature within the  
16      range from about 0°C to about 100°C. The components will be  
17      combined, preferably, in an aromatic hydrocarbon solvent, most  
18      preferably toluene. Nominal holding times within the range from  
19      about 10 seconds to about 60 minutes will be sufficient to produce  
20      both the preferred and most preferred catalysts of this invention.

21           In a preferred and most preferred embodiment of this  
22       invention, the catalyst, immediately after formation, will be used  
23       to polymerize one or more lower  $\alpha$ -olefins, particularly ethylene  
24       and propylene, most preferably ethylene, at a temperature within  
25       the range from about 0°C to about 100°C and at a pressure within  
26       the range from about 15 to about 500 psig. The monomers will be  
27       maintained at polymerization conditions for a nominal holding time  
28       within the range from about 1 to about 60 minutes and the catalyst  
29       will be used at a concentration within the range of about  $10^{-5}$  to  
30       about  $10^{-1}$  moles per liter of solvent or diluent.

31           Having thus broadly described the present invention and a  
32       preferred and most preferred embodiment thereof, it is believed  
33       that the same will become even more apparent by reference to the  
34       following examples. It will be appreciated, however, that the  
35       examples are presented solely for purposes of illustration and  
36       should not be construed as limiting the invention. In the examples  
37       wherein an active catalyst was isolated and identified, the

1 analysis was by solid-state  $^{13}\text{C}$  NMR spectroscopy and solution  
2  $^1\text{H}$  NMR spectroscopy.

3 EXAMPLE 1

4 In this example, an active olefin polymerization catalyst  
5 was prepared and isolated by combining 1.0 g of bis(pentamethyl-  
6 cyclopentadienyl)zirconium dimethyl in 50 ml toluene and then  
7 adding 0.82 g of tri(*n*-butyl)ammonium 7,8-dicarbaundecaborate(12).  
8 The mixture was stirred at room temperature for 30 minutes, the  
9 solvent was evaporated to half its original volume and pentane  
10 added to the point of cloudiness. After cooling at -20°C  
11 overnight, a yellow solid was filtered off, washed with pentane and  
12 dried. The yield of active catalyst was 0.75 g. A portion of this  
13 product was analyzed and identified as bis(pentamethylcyclo-  
14 dienyl)methyl(dodecahydrido-7,8-dicarbaundecaborato)zirconium.

15 EXAMPLE 2

16 In this example, an active olefin polymerization catalyst  
17 was prepared by dissolving 1.2 g of bis(pentamethylcyclo-  
18 pentadienyl)zirconium dimethyl in 100 ml pentane and then adding  
19 dropwise 5 ml of a toluene solution containing 0.38 g of  
20 7,8-dicarbaundecaborane(13). A bright yellow solid precipitated  
21 from solution. After thirty minutes, the solid was filtered off,  
22 washed with pentane and dried. The yield of product was 0.95 g. A  
23 portion of the product was analyzed and identified as bis(penta-  
24 methylcyclopentadienyl)methyl(dodecahydrido-7,8-dicarbaundecaborato)  
25 zirconium, the same active catalyst produced in Example 1.

26 EXAMPLE 3

27 In this example, an active olefin polymerization catalyst  
28 was prepared by dissolving 0.425 g of bis(ethyltetramethylcyclo-  
29 pentadienyl)zirconium dimethyl in 60 ml of pentane and adding  
30 dropwise 5 ml of a toluene solution containing 0.125 g of  
31 7,8-dicarbaundecaborane(13). A bright yellow solid precipitated  
32 from solution. After fifteen minutes, the solid was filtered off,  
33 washed with pentane and dried. The yield of product was 0.502 g.  
34 A portion of the product was analyzed and identified as  
35 bis(ethyltetramethylcyclopentadienyl)methyl(dodecahydrido-7,8-di-  
36 carbaundecaborato)zirconium.

1    EXAMPLE 4

2            In this example, ethylene was polymerized using a portion  
3    of the catalyst produced in Example 2 by dissolving 50 mg of the  
4    catalyst in 100 ml of toluene and transferring the catalyst  
5    solution under a nitrogen atmosphere into a stirred, steel 1 liter  
6    autoclave which was previously flushed with nitrogen. The  
7    autoclave was pressured with 300 psig ethylene and stirred at  
8    60°C. After thirty minutes, the reactor was vented and opened.  
9    The yield of linear polyethylene formed was 22.95 g.

10   EXAMPLE 5

11           In this example, ethylene was polymerized with the  
12   catalyst produced in Example 3 by dissolving 50 mg of the catalyst  
13   in 100 ml of toluene and transferring the catalyst solution under a  
14   nitrogen atmosphere into a stirred, steel 1 liter autoclave which  
15   was previously flushed with nitrogen. The autoclave was pressured  
16   with 400 psig ethylene and stirred at 40°C. After one hour, the  
17   reactor was vented and opened. The yield of linear polyethylene  
18   formed was 74.6 g.

19   EXAMPLE 6

20           In this example, ethylene was again polymerized with a  
21   portion of the catalyst produced in Example 2 by dissolving 75 mg  
22   of the catalyst in 100 ml of chlorobenzene and transferring under a  
23   nitrogen atmosphere into a stirred, steel 1 liter autoclave which  
24   was previously flushed with nitrogen. The autoclave was pressured  
25   with 150 psig ethylene and stirred at 40°C. After twenty minutes,  
26   the reactor was vented and opened. The yield of linear poly-  
27   ethylene formed was 3.3 g.

28   EXAMPLE 7

29           In this example, ethylene was polymerized with an active  
30   catalyst formed in situ by dissolving 80 mg of bis(pentamethyl-  
31   cyclopentadienyl)zirconium dimethyl and 35 mg of 1,2-dicarbaun-  
32   decaborane(13) in 20 ml of dichloromethane. Ethylene was then  
33   bubbled through the solution at atmospheric conditions for one  
34   minute and the slurry then poured into an excess of ethanol. The  
35   polyethylene formed was filtered off, washed with water and acetone  
36   and dried. The yield of polyethylene was 1.6 g.

1    EXAMPLE 8

2            In this example, an active catalyst was prepared by  
3    reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (46 mg)  
4    with octadecaborane(22) (20 mg) in toluene (5 ml). There was  
5    considerable gas evolution. On passing ethylene through the  
6    solution for one minute, the solution grew hot. The vial was  
7    opened and acetone added to precipitate the polymer, which was  
8    filtered off, washed with acetone, and dried. The yield of polymer  
9    isolated was 0.32 g.

10    EXAMPLE 9

11           In this example, an active catalyst was prepared by  
12    reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (40 mg)  
13    with tri(n-butyl)ammonium tridecahydrido-7-carbaundecaborate (30  
14    mg) in toluene (50 ml) in a serum-capped round-bottomed flask. The  
15    solution turned from colorless to orange-yellow. On passing  
16    ethylene through the solution for 1 minute, the solution grew hot  
17    as polymer precipitated from solution.

18    EXAMPLE 10

19           In this example, an active catalyst was prepared in an NMR  
20    tube by combining 50 mg of bis(pentamethylcyclopentadienyl)  
21    zirconium dimethyl and 40 mg of tri(n-butyl)ammonium 1-carbado-  
22    decaborate in 1 ml of hexadeuteriobenzene and placing the solution  
23    into the NMR tube. The disappearance of starting material was then  
24    observed by <sup>1</sup>H NMR spectroscopy and when the starting materials  
25    had disappeared ethylene was injected into the NMR tube. Solid  
26    polymer precipitated from the solution.

27    EXAMPLE 11

28           In this example, an active catalyst was again prepared in  
29    an NMR tube by dissolving 100 mg of bis[1,3-bis(trimethylsilyl)  
30    cyclopentadienyl]zirconium dimethyl and 60 mg of tri(n-butyl)  
31    ammonium 1-carbadodecarborate in 1 ml of hexadeuteriobenzene and  
32    then placing the solution into the NMR tube. The disappearance of  
33    starting materials was observed in the <sup>1</sup>H NMR spectrum. When all  
34    of the starting zirconium compound had disappeared, ethylene was  
35    injected into the tube and solid polymer precipitated from solution.

1    EXAMPLE 12

2            In this example, an active catalyst was again formed in an  
3            NMR tube by dissolving 100 mg of (pentamethylcyclopentadienyl)  
4            [1,3-bis(trimethylsilyl)cyclopentadienyl]zirconium dimethyl and 70  
5            mg of tri(n-butyl)ammonium 1-carbadodecaborate in 1 ml of  
6            hexadeuteriobenzene and then placing the solution in the NMR tube.  
7            Disappearance of starting material was followed by <sup>1</sup>H NMR  
8            spectrum and when all of the starting zirconium compound had  
9            disappeared ethylene was injected into the tube. Solid ethylene  
10           polymer then precipitated from solution.

11    EXAMPLE 13

12           In this example, an active catalyst was prepared by  
13           suspending 80 mg bis(pentamethylcyclopentadienyl)zirconium dimethyl  
14           and 50 mg of bis[tri(n-butyl)ammonium]dodecaborate in 7 ml of  
15           toluene in a serum capped vial. On mixing, the suspension turned  
16           from colorless to yellow-green. Bubbling ethylene through the  
17           solution for 30 seconds caused a white polymer to form as the  
18           solution became warm. The vial was opened and the polymer  
19           precipitated with ethanol. The yield of polyethylene was 0.13 g.

20    EXAMPLE 14

21           In this example, an active catalyst was prepared by  
22           reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (45 mg)  
23           with tri(n-butyl)ammonium undecahydrido-1-carbaundecaborate (30 mg)  
24           in toluene (5 ml) in a serum-capped vial. The solution turned from  
25           colorless to yellow. On passing ethylene through the solution for  
26           30 seconds, the solution grew hot as polymer precipitated.

27    EXAMPLE 15

28           In this example, an active catalyst was prepared by  
29           suspending 80 mg of bis(pentamethylcyclopentadienyl)zirconium  
30           dimethyl and 90 mg of N,N-dimethylanilinium bis(7,8-dicarbaun-  
31           decaborato)cobaltate(III) in 5 ml of toluene in a serum-capped  
32           vial. The yellow solution turned orange-violet with gas  
33           evolution. On passing ethylene through the solution for 30  
34           seconds, the solution turned deep violet with considerable  
35           evolution of heat and became viscous. The vial was opened and the  
36           solids precipitated with ethanol. These were washed with 10%

1 aqueous sodium hydroxide solution, ethanol, acetone and hexane.  
2 The yield of polyethylene was 0.41 g.

3 EXAMPLE 16

4 In this example, an active catalyst was prepared by  
5 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (40 mg)  
6 with N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)ferrate(III)  
7 (45 mg) in toluene (10 ml) in a serum-capped vial. On passing  
8 ethylene through the solution, the mixture grew hot as polymer  
9 formed. The vial was opened and the contents diluted with acetone,  
10 then filtered and dried. The yield of polymer isolated was 0.33 g.

11 EXAMPLE 17

12 In this example, an active catalyst was prepared by  
13 reacting bis(pentamethylcyclopentadienyl)zirconium dimethyl (40 mg)  
14 with tri(n-butyl)ammonium bis(7,8-dicarbaundecaborato)nickelate  
15 (III) (45 mg) in toluene (30 ml) in a serum-capped round-bottomed  
16 flask. Ethylene was passed through the solution for one minute.  
17 The solution grew hot as polymer precipitated from solution. The  
18 flask was opened and the contents diluted with acetone. The solid  
19 polymer was filtered off, washed with acetone, and dried. The  
20 yield of isolated polymer was 0.48 g.

21 EXAMPLE 18

22 In this example, an active catalyst was prepared by  
23 suspending 100 mg of bis(methylcyclopentadienyl)zirconium dihydride  
24 and 180 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
25 cobaltate(III) in 100 ml of toluene in a 250 ml round bottomed  
26 flask capped with a rubber septum. Ethylene was bubbled through  
27 the solution for 10 minutes. The flask was opened, the contents  
28 poured into hexane, filtered off and dried. The yield of polymer  
29 was 2.98 g.

30 EXAMPLE 19

31 In this example, an active catalyst was prepared by  
32 suspending 105 mg of bis[1,3-bis(trimethylsilyl)cyclopenta-  
33 dienyl]zirconium dimethyl and 90 mg of N,N-dimethylanilinium  
34 bis(7,8-dicarbaundecaborato)cobaltate(III) in 50 ml of toluene in a  
35 100 ml round bottomed flask capped with a rubber septum. Ethylene  
36 was bubbled through the solution for 10 minutes. The flask was

1       opened and the contents poured into ethanol and evaporated. The  
2       yield of polymer was 2.7 g.

3       EXAMPLE 20

4           In this example, an active catalyst was prepared by  
5       stirring 50 mg of bis(cyclopentadienyl)zirconium dimethyl and 90 mg  
6       of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III)  
7       in 50 ml of toluene in a 100 ml round bottomed flask capped with a  
8       rubber septum. On passing ethylene through the solution, no  
9       obvious reaction was observed for one minute, after which a  
10      pronounced turbidity could be seen. After 10 minutes, the flask  
11      was opened, the contents diluted with ethanol and evaporated. The  
12      yield of polymer was 1.9 g.

13       EXAMPLE 21

14           In this example, ethylene was polymerized by reacting 69  
15      mg of bis(cyclopentadienyl)hafnium dimethyl with 90 mg of  
16      N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III) in  
17      50 ml of toluene in a septum-capped round bottomed flask. On  
18      passing ethylene through the solution, a pronounced turbidity  
19      appeared after 30 seconds as the solution grew hot. After 10  
20      minutes, the solution was poured into acetone and the polymer  
21      filtered off and dried. The yield of linear polyethylene was 2.2 g.

22       EXAMPLE 22

23           In this example, ethylene was polymerized by reacting 50  
24      mg of bis(trimethylsilylcyclopentadienyl)hafnium dimethyl with 45  
25      mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
26      cobaltate(III) in 5 ml of toluene in a serum-capped vial. On  
27      passing ethylene through the solution, polymer formed as the  
28      mixture grew hot. After 1 minute, the vial was opened and the  
29      contents diluted with acetone and filtered off. The yield of  
30      linear polyethylene was 0.35 g.

31       EXAMPLE 23

32           In this example, ethylene and 1-butene were copolymerized  
33      in a toluene diluent by adding under a nitrogen atmosphere to a 1  
34      liter stainless-steel autoclave, previously flushed with nitrogen  
35      and containing 400 ml of dry, oxygen-free toluene, 35 ml of a  
36      toluene solution containing a catalyst prepared in situ from 50 mg  
37      of bis(cyclopentadienyl)zirconium dimethyl and 45 mg of

1 N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III).  
2 1-Butene (200 ml) was added to the autoclave, which was further  
3 pressurized with 120 psig of ethylene. The autoclave was stirred  
4 at 50° for 30 minutes, then cooled and vented. The contents were  
5 dried under a stream of air. The weight of the polymer isolated  
6 was 44.7 g. The melting point of the polymer was 117°C and  
7 analysis by infra-red spectroscopy indicated that there were about  
8 17 ethyl branches per 1000 carbon atoms.

9 EXAMPLE 24

10 In this example, ethylene and 1-butene were copolymerized  
11 in a toluene diluent by adding under a nitrogen atmosphere to a 1  
12 liter stainless-steel autoclave, previously flushed with nitrogen  
13 and containing 400 ml of dry, oxygen-free toluene, 50 ml of a  
14 catalyst solution in toluene containing 70 mg of bis(cyclopenta-  
15 dienyl)hafnium dimethyl and 45 mg of N,N-dimethylanilinium  
16 bis(7,8-dicarbaundecaborato)cobaltate(III). 1-Butene (200 ml) was  
17 added to the autoclave, which was further pressurized with 120 psig  
18 of ethylene. The autoclave was stirred at 50° for 20 minutes, then  
19 cooled and vented. The contents were dried under a stream of air.  
20 The yield of isolated polymer was 75.1 g. The melting point of the  
21 polymer was 109°C and analysis by infra-red spectroscopy indicated  
22 that there were about 29 ethyl branches per 1000 carbon atoms.

23 EXAMPLE 25

24 In this example, ethylene was polymerized by reacting 66  
25 mg of 1-bis(cyclopentadienyl)titana-3-dimethylsilacyclobutane and  
26 88 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
27 cotateate(III) in 25 ml of toluene in a serum-capped round-bottomed  
28 flask. The solution darkened on passage of ethylene through it.  
29 After 10 minutes, the flask was opened and the contents diluted  
30 with ethanol. The polymer was filtered off, washed with ethanol  
31 and acetone, and dried. The yield of polyethylene isolated was  
32 0.09 g.

33 EXAMPLE 26

34 In this example, ethylene was polymerized by reacting 61  
35 mg of 1-bis(cyclopentadienyl)zircona-3-dimethylsilacyclobutane and  
36 87 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
37 cotateate(III) in 20 ml of toluene in a serum-capped round-bottomed

1 flask. On passing ethylene through the solution, polymer  
2 precipitated as the solution grew warm. After 10 minutes, the vial  
3 was opened and the contents diluted with ethanol. The precipitate  
4 was filtered off, washed with ethanol, and dried. The yield of  
5 polyethylene isolated was 1.41 g.

6 EXAMPLE 27

7 In this example, ethylene was polymerized by reacting 82  
8 mg of 1-bis(cyclopentadienyl)hafna-3-dimethylsilacyclobutane and 88  
9 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
10 cobaltate(III) in 20 ml of toluene in a serum-capped round-bottomed  
11 flask. On passing ethylene through the solution, polymer  
12 precipitated as the solution grew hot. After 5 minutes, the flask  
13 was opened and the contents diluted with ethanol. The polymer was  
14 filtered off, washed with ethanol, and dried. The yield of  
15 polyethylene isolated was 1.54 g.

16 EXAMPLE 28

17 In this example, ethylene was polymerized by reacting 67  
18 mg of bis(cyclopentadienyl)zirconium(2,3-dimethyl-1,3-butadiene)  
19 and 88 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
20 cobaltate(III) in 50 ml of toluene in a serum-capped bottle.  
21 Ethylene was passed through the solution, which gradually grew  
22 warm. After 15 minutes, the bottle was opened and the contents  
23 diluted with ethanol. The polymer was filtered off, washed with  
24 ethanol, and dried. The yield of polymer isolated was 1.67 g.

25 EXAMPLE 29

26 In this example, ethylene was polymerized by reacting 40  
27 mg of bis(cyclopentadienyl)hafnium(2,3-dimethyl-1,3-butadiene) with  
28 43 mg of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)  
29 cobaltate(III) in 50 ml of toluene in a serum-capped bottle.  
30 Ethylene was passed through the solution, which became turbid  
31 within 30 seconds. After 20 minutes, the bottle was opened and the  
32 contents diluted with ethanol. The solid polymer was filtered off,  
33 washed with ethanol, and dried. The yield of polyethylene isolated  
34 was 0.43 g.

35 EXAMPLE 30

36 In this example, ethylene was polymerized by reacting 55  
37 mg of (pentamethylcyclopentadienyl)(tetramethyl-eta<sup>1</sup>-methylene

1 -eta<sup>5</sup>-cyclopentadienyl)zirconium phenyl and 45 mg of N,N-di-  
2 methylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III) in 20 ml  
3 of toluene in a serum-capped round-bottomed flask. On passing  
4 ethylene through the solution, polymer formed almost instantly and  
5 much heat was evolved. After 5 minutes, the flask was opened and  
6 the contents diluted with ethanol. The precipitate was filtered  
7 off, washed with acetone, and dried. The yield of polyethylene  
8 isolated was 0.55 g.

9 EXAMPLE 31

10 In this example, ethylene was polymerized by reacting 80  
11 mg of (pentamethylcyclopentadienyl)(tetramethylcyclopentadienyl-  
12 methylene)hafnium benzyl and 60 mg of N,N-dimethylanilinium  
13 bis(7,8-dicarbaundecaborato)cobaltate(III) in 50 ml of toluene in a  
14 serum-capped bottle. Ethylene was passed through the solution for  
15 10 minutes. Polymer precipitated as the solution grew warm. The  
16 bottle was opened and the contents diluted with ethanol. The solid  
17 polymer was filtered off, washed with acetone, and dried. The  
18 yield of polyethylene isolated was 0.92 g.

19 EXAMPLE 32

20 In this example, ethylene was polymerized by reacting 0.42  
21 g of bis(trimethylsilylcyclopentadienyl)hafnium dimethyl with 0.08  
22 g N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)cobaltate(III)  
23 in 10 ml of toluene. A portion of this solution (0.4 ml) was  
24 injected under a pressure of 3000 bar of Isopar into an autoclave  
25 pressurized to 1500 bar with ethylene and heated to 160°. After 5  
26 seconds the contents of the autoclave were discharged. Linear  
27 polyethylene (2.1 g) with a weight-average molecular weight of  
28 144,000 and a molecular weight distribution of 2.9 was isolated.

29 While the present invention has been described and  
30 illustrated by reference to particular embodiments thereof, it will  
31 be appreciated by those of ordinary skill in the art that the same  
32 lends itself to variations not necessarily illustrated herein. For  
33 this reason, then, reference should be made solely to the appended  
34 claims for purposes of determining the true scope of the present  
35 invention.

## CLAIMS:

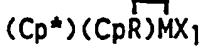
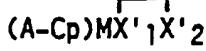
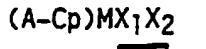
1. Method for preparing a catalyst comprising the steps of:

(a) combining, in a suitable solvent or diluent, at least one first compound consisting of a bis(cyclopentadienyl)metal compound containing at least one substituent capable of reacting with a proton, said metal being selected from the group consisting of titanium, zirconium and hafnium and at least one second compound comprising a cation, capable of donating a proton, and an anion containing a plurality of boron atoms which is bulky, labile and capable of stabilizing the metal cation formed as a result of the reaction between the two compounds;

(b) maintaining the contacting in step (a) for a sufficient period of time to permit the proton provided by the cation of said second compound to react with said substituent contained in said metal compound; and

(c) recovering an active catalyst as a direct product or as a decomposition product of one or more of said direct products from Step (b).

2. Method according to Claim 1 wherein said bis(cyclopentadienyl)metal compound may be represented by the following general formulae:

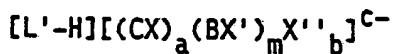


Wherein:

M is a metal selected from the group consisting of titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either  $(Cp)(Cp^*)$  or  $Cp-A'-Cp^*$  and Cp and Cp\* are the same or different substituted or unsubstituted cyclopentadienyl radicals, optionally two independently substituted or unsubstituted radicals; A' is a covalent bridging group

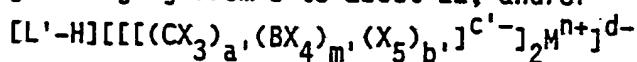
containing a Group IV-A element; L is an olefin, diolefin or aryne ligand;  $X_1$  and  $X_2$  are, independently, selected from the group consisting of hydride radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, optionally two lower alkyl substituents or two hydrides, organo-metalloid radicals and the like;  $X'_1$  and  $X'_2$  are joined and bound to the metal atom to form a metallacycle, in which the metal,  $X'_1$  and  $X'_2$  form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and R is a substituent on one of the cyclopentadienyl radicals which is also bound to the metal atom.

3. Method according to Claim 1 or Claim 2 wherein said second compound may be represented by one of the following general formulae:



Wherein:

$L'$ -H is either  $H^+$ , ammonium or a substituted ammonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B and C are, respectively, boron and carbon; X,  $X'$  and  $X''$  are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metalloid radicals and the like; a and b are integers  $\geq 0$ ; c is an integer  $\geq 1$ ;  $a + b + c =$  an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22; and/or



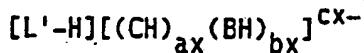
Wherein:

$L'$ -H is either  $H^+$ , ammonium or a substituted-ammonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up

to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C, M and H are, respectively, boron, carbon, a transition metal and hydrogen;  $X_3$ ,  $X_4$  and  $X_5$  are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metallocloid radicals and the like;  $a'$  and  $b'$  are the same or a different integer  $\geq 0$ ;  $c'$  is an integer  $\geq 2$ ;  $a + b' + c' =$  an even-numbered integer from 4 to about 8;  $m'$  is an integer from 6 to about 12;  $n$  is an integer such that  $2c' - n = d$ ; and  $d$  is an integer  $\geq 1$ .

4. Method according to any of the preceding claims wherein the contacting of step (a) is accomplished at a temperature within the range from about  $-100^{\circ}\text{C}$  to about  $300^{\circ}\text{C}$ , preferably at from 0 to 45,000 psig.

5. Method according to any of the preceding claims wherein said second compound is represented by the general formula:



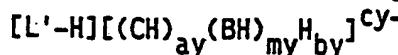
Wherein:

$L'$ -H is either  $\text{H}^+$ , ammonium or a substituted-ammonium optionally tri-substituted radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C, and H are, respectively, boron, carbon and hydrogen;  $ax$  is either 0 or 1;  $cx$  is either 2 or 1;  $ax + cx = 2$ ; and  $bx$  is an integer ranging from 10 to 12.

6. Method according to Claim 6 wherein said second compound is selected from the group consisting of bis[tri(n-butyl) ammonium] dodecaborate and tri(n-butyl)ammonium 1-carbaundeca or 1-carbadodecaborate and said first compound is selected from the group consisting of bis(pentamethylcyclopentadienyl)zirconium

dimethyl, (pentamethylcyclopentadienyl) (cyclopentadienyl)zirconium dimethyl, and [1,3-bis(trimethylsilyl)cyclopentadienyl]zirconium dimethyl.

7. Method according to any of Claims 1 to 4 wherein said second compound is represented by the following general formula:

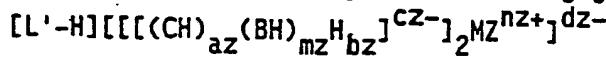


Wherein:

$L'$ -H is either  $H^+$ , ammonium or a substituted-ammonium, optionally tri-substituted, radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C and H are, respectively, boron, carbon and hydrogen; ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3; ay + by + cy = 4; and mx is an integer from 9 to 18.

8. Method according to Claim 7 wherein said second compound is selected from the group consisting of tri(n-butyl) ammonium 7,8-dicarbaundecaborate and tri(n-butyl)ammonium tridecahydrido-7-carbaundecaborate in which case preferably the first compound is bis(pentamethylcyclopentadienyl)zirconium dimethyl and/or wherein  $L'$ -H is  $H^+$ , preferably 7,8-dicarbaundecaborane(13) or octadecaborane(22) in which case optionally said first compound is selected from the group consisting of bis(pentamethylcyclopentadienyl)zirconium dimethyl and bis(ethyltetramethylcyclopentadienyl)zirconium dimethyl.

9. Method according to any of Claims 1 to 4 wherein said second compound may be represented by the following general formula:



Wherein:

$L'$ -H is either  $H^+$ , ammonium or a substituted ammonium radical having up to 3 hydrogen atoms replaced with a

hydrocarbyl or substituted-hydrocarbyl radical, a phosphonium or substituted-phosphonium radical having up to 3 hydrogen atoms replaced with a hydrocarbyl or substituted-hydrocarbyl radical and the like; B, C, H and MZ are, respectively, boron, carbon, hydrogen and a transition metal; az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from 9 to 11; az + bz + cz = 4; and nz and dz are, respectively, 2 & 2 or 3 & 1.

10. Method according to Claim 9 wherein said second compound is N,N-dimethylanilinium bis(undecahydrido-7,8-dicarbaundecaborato) cobaltate(III) and/or wherein said first compound is selected from the group consisting of 1-bis(cyclopentadienyl)titana-3-dimethylsilacyclobutane, 1-bis(cyclopentadienyl)zirconia-3-dimethylsilacyclobutane, and 1-bis(cyclopentadienyl)hafnia-3-dimethylsilacyclobutane, bis(cyclopentadienyl) zirconium (2,3-dimethyl-1,3-butadiene) and bis(cyclopentadienyl) hafnium(2,3-dimethyl-1,3-butadiene), (pentamethylcyclopentadienyl) (tetramethylcyclopentadienyl-methylene)zirconium phenyl and (pentamethylcyclopentadienyl) (tetramethylcyclopentadienylmethylene) hafnium benzyl; or wherein said second compound is selected from the group consisting of N,N-dimethylanilinium bis(7,8-dicarbaundecaborato)nickelate(III) and N,N-dimethylanilinium bis(7,8-dicarbaundecaborato) ferrate(III) in which case preferably said first compound is bis(pentamethylcyclopentadienyl)zirconium dimethyl.

11. Method for polymerizing an  $\alpha$ -olefin, a diolefin and/or an acetylenically unsaturated compound containing from 2 to about 18 carbon atoms either alone or in combination with one or more other monomers comprising the steps of:

(a) contacting at a temperature within the range from about -100°C to about 300°C and at a pressure within the range from about 0 to about 45,000 psig. an olefin, diolefin and/or an acetylenically unsaturated monomer either alone or in combination with one or more other monomers in a suitable

carrier, solvent or diluent with a catalyst prepared previously or in situ during polymerization by a method according to any of the preceding claims;

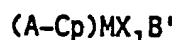
(b) continuing the contacting of step (a) for a sufficient period of time to polymerize at least a portion of said olefin;

(c) recovering a polymer product.

12. A catalyst prepared by a method according to any of Claims 1 to 10.

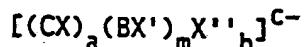
13. Polyolefin produced in accordance with the method of claim 11.

14. Composition of matter containing compounds represented by the following general formula:



Wherein:

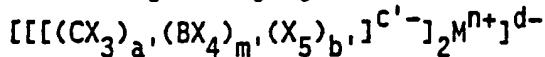
M is a metal selected from the group consisting of titanium (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either  $(Cp)(Cp^*)$  or  $CP-A'-Cp^*$  and Cp and Cp\* are the same or different substituted or unsubstituted cyclopentadienyl radicals; A' is a covalent bridging group containing a Group IV-A element;  $X_1$  is selected from the group consisting of hydride radicals, hydrocarbyl radicals, organo-metallocid radicals and the like; and B' is a compatible non-coordinating anion which may be represented by one of the following general formulae:



Wherein:

B and C are, respectively, boron and carbon; X, X' and X'' are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metallocid radicals and the like; a and b are integers  $\geq 0$ ; c is an integer  $\geq 1$ ;

$a + b + c =$  an even-numbered integer from 2 to about 8;  
and  $m$  is an integer ranging from 5 to about 22; and 34



Wherein:

B, C and M are, respectively, boron, carbon and a transition metal;  $X_3$ ,  $X_4$  and  $X_5$  are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals, organo-metallocid radicals and the like;  $A'$  and  $b'$  are the same or a different integer  $\geq 0$ ;  $C'$  is an integer  $\geq 2$ ;  $a' + b' + c' =$  an even-numbered integer from 4 to about 8;  $m'$  is an integer from 6 to about 12;  $n$  is an integer such that  $2c' - n = d$ ; and  $d$  is an integer  $\geq 1$ .

15. Composition of matter according to Claim 14 wherein (A-Cp) is a bis(peralkyl-substituted cyclopentadienyl); X is an alkyl group; B' is (dodecahydrido-7,8-dicarbaundecaborato) and M is zirconium and wherein each of the alkyl groups in the peralkyl-substituted cyclopentadienyl radicals are, independently,  $C_1-C_{20}$  alkyl radicals and the alkyl group is a  $C_1-C_{20}$  alkyl radical, the peralkyl substitution being preferably pentamethyl or ethyltetramethyl and the alkyl radical being preferably a methyl radical.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 88/00222

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>4</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC <sup>4</sup> : C 08 F 4/64; C 08 F 4/76; C 08 F 10/00; C 07 F 17/00

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System	Classification Symbols
IPC <sup>4</sup>	C 08 F; C 07 F

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	Journal of the Chemical Society, Chemical Communications, 1986, M. Bochmann et al.: "Synthesis and insertion reactions of cationic alkylbis(cyclopentadienyl)titanium complexes", pages 1610-1611 see the whole abstract cited in the application --	1
A	EP, A, 0200351 (MITSUI PETROCHEM) 5 November 1986 see the whole document cited in the application --	1
A	US, A, 3231593 (W. HAFNER et al.) 25 January 1966 see claims; column 5, line 71 - column 7, line 7; examples -----	1

\* Special categories of cited documents: 10

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

14th April 1988

Date of Mailing of this International Search Report

19 MAY 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8800222  
SA 20798

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 09/05/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0200351	05-11-86	JP-A- 61221207 US-A- 4704491 JP-A- 62121710	01-10-86 03-11-87 03-06-87
US-A- 3231593		None	

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